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RESEARCH STUDY OF CHEMISPORTION BY MAGNETO ABSORPTION

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AERONAUTICAL SYSTEMS DIVISION
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PROJECT No. 7022, TASK No. 73664

(Prepared under Contract No. AF 33(616)-6287 by
Varian Associates, Palo Alto, California;
D. P. Hollis, Author)

NOTICES

FOREWORD

This report was prepared by Varian Associates, Palo Alto, California, under USAF Contract No. AF 33(616)-6287. The contract was initiated under Project No. 7022, "Research on Interface Phenomena", Task No. 73664, "Interaction of Surfaces with Extreme Environments". The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with R. J. Barton acting as project scientist.

The studies presented were conducted from February 1959 through December 1960.

Donald P. Hollis was the engineer responsible for research activity of Varian Associates, L. H. Piette was project manager, and Dr. P. W. Selwood served as project Consultant.

ABSTRACT

The effect of adsorbed hydrogen on the magnetic losses in finely divided nickel at 3.7 and 13 Mc/sec. has been studied. The increased sensitivity at these frequencies is attributed to a difference in relaxation times for particles of different sizes.

Experiments designed to detect the effect of adsorbed hydrogen on the microwave absorption of iron and nickel single crystals are described. Possible reasons for the lack of a clear-cut effect are discussed.

Ferromagnetic resonance spectra of finely divided nickel are described. The effects of adsorbed hydrogen on the intensity, g-value and line width of the resonance are discussed. It is demonstrated that the well-known magnetic effects of chemisorbed hydrogen on nickel, which have been measured at static and low frequency fields, can be observed also by magnetic resonance and with a sensitivity at least 10^5 greater, in terms of weight of metal required.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

E.M. Kennedy Jr.

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I. PURPOSE

The purpose of the program undertaken on Contract No. AF 33(616)-6287 for the Wright Air Development Division was to investigate the type of adsorption of gas or vapor by studying the magnetic absorption of metals in the super paramagnetic region.

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II. INTRODUCTION

Adsorption of gases on solid surfaces is important in corrosion, embrittlement, and heterogeneous catalysis and has therefore been the subject of numerous studies. It is believed that chemisorption is an essential step in the surface reaction and that the chemisorbed species are held to the surface by chemical valence bonds. The chemisorption bond has been studied by many of the standard means such as optical absorption, X-ray diffraction, and electron diffraction. However, as a consequence of the small concentration of the adsorbed phase relative to the solid adsorbent phase, these techniques have not proved very useful when applied to this problem. Studies of the effects of chemisorption on the electronic properties of the solids have usually proved more successful than those in which a direct examination of the chemisorption bond has been attempted.

In the case of semiconductors and insulators where the number of electrons contributing to the conduction properties is small, significant changes in electrical properties of the adsorbent can be observed as a result of chemisorption. In the case of metals, however, difficulty is encountered because of the large number of conduction electrons. For hydrogen chemisorption on nickel, the conduction electrons have been found to play only a minor role, and a number of workers has speculated that the unpaired three-d electrons have special importance.[1] The experiments of Selwood and co-workers[2] who found that

the chemisorption of hydrogen leads to a decrease in the magnetization of nickel-silica catalysts, have indicated that this is the case. Since the saturation magnetization of nickel results from the unpaired electron spins in the three-d band, the decrease in magnetization on chemisorption indicates a filling of previously unoccupied d-levels. One of the objectives of the present work is to extend the static and low-frequency magnetic results by investigating the effect of hydrogen chemisorption on nickel at frequencies in the radio and microwave range.

III. BRIEF REVIEW OF OTHER STUDIES OF THE NICKEL HYDROGEN SYSTEM

Before discussing in more detail the ideas and objectives which have led to the present work, a brief review will be given of the more important research findings relating to the nickel-hydrogen chemisorption bond.

This review and the author's work which follows will be concerned chiefly with the investigation of the nickel system before and after chemisorption of hydrogen and hence will be concerned with equilibrium phenomena. Little will be said concerning the large amount of kinetic data available on the chemisorption process on the reactions which occur when the nickel is used as a catalyst for some particular reaction. In preparing this review, much use has been made of the more complete previous reviews by Dietz[30] and Gundry and Tompkins.[3]

A. HEATS OF ADSORPTION

Heats of adsorption of hydrogen on nickel have been determined in two ways: 1) by direct calorimetry, 2) from equilibrium pressure measurements using the Clausius-Clapeyron equation. The maximum values measured are about 40 K cal/mole and were obtained for adsorption on thin nickel films.[4] For nickel powders, the initial heats of adsorption are generally between 20 and 30 k cal/mole.[5, 6] In every case, the incremental heat of adsorption has been found to decrease with increasing surface coverage. No generally

accepted explanation of this effect has yet been proposed, although there has been considerable speculation as to its origin. Roberts[7] suggested that interactions among the adsorbed species which increase with increasing coverage could account for the observed decrease in heats. Trapnell,[8] however, has presented arguments showing that this effect is too small to account for the magnitude of the decrease. De Boer[9] has argued to the effect that the explanation lies in the change in work function of the adsorbing metal. A third argument, which seems to be most generally accepted attributes the effect to surface heterogeneity; a distribution of adsorption sites among which the energy of adsorption differs. From hydrogen-deuterium exchange reactions on nickel-silica catalysts, Schuit and van Reijen[5] have concluded that these surfaces are heterogeneous.

B. INFRARED SPECTROSCOPY

Pliskin and Eischens[10] have investigated the adsorption of hydrogen on disperse platinum and nickel systems by infrared spectroscopy. They have observed two partially superimposed bands for hydrogen on platinum but for unexplained reasons no band for hydrogen on nickel has been observed.

C. SURFACE POTENTIALS AND ELECTRICAL CONDUCTIVITY

The results obtained from surface potential and conductivity measurements on their nickel films are sufficiently similar that they

can be discussed together. Mignolet[11, 12] has done most of the work on surface potentials, while several workers have studied the electrical conductivities of thin films.[13, 14, 15]

Both the work function and the conductivity increase with hydrogen adsorption at low coverages, but the opposite effect has been observed at higher coverages. These results have been taken by both Sachtler and Dorgelo,[14] and Mignolet to be evidence for two types of chemisorbed hydrogen, one of which is negatively charged and which occupies sites between surface nickel atoms while the second type is thought to carry a positive charge and to occur on top of the surface nickel atoms. This idea is also supported by field electron microscope studies of nickel by Sachtler,[13] and by Roginskii and Tretyakov,[16] in which light spots appearing in the emission pattern at high coverage indicated points of decreased work function.

Surface potential data has been used to calculate a dipole moment of .022 Debye for the nickel-hydrogen bond, with the negative pole directed outward from the surface. This is considered evidence that the nickel-hydrogen bond is covalent, since one expects the dipole moment of a completely ionic bond to be of the order 10 Debye.

D. FIELD EMISSION MICROSCOPY

Gomer and his associates have carried out field emission microscope studies on the nickel-hydrogen system.[17] In agreement with the work above, the Gomer group found that the work function decreased

on coverage of the surface with hydrogen. The hydrogen layer is found to be immobile at temperatures below 240°K. At liquid helium temperatures, a field dependent change occurs in the chemisorbed layer, which was attributed to a shift in the equilibrium between atomically adsorbed and molecularly adsorbed hydrogen. The molecular species was considered to have a small heat of adsorption and to be attached directly above the nickel atoms. The work function was observed to increase after the transition to the atomic state. Finally, these workers derived an activation energy of desorption by measuring the "clean-up" times for the hydrogen covered nickel tip as a function of temperature. For low coverages, a value of 46 ± 4 k cal/mole H_2 was obtained. It is the contention of these workers that while this figure represents an activation energy, it can be taken as the heat of adsorption, since the activation energy of adsorption can be neglected, in view of the nearly instantaneous rate of adsorption. This figure is near the one measured by Klemperer and Stone.[4]

E. MAGNETIC STUDIES

The effect of chemisorbed hydrogen on the magnetization of nickel-silica catalysts was discovered by P. W. Selwood and his associates at Northwestern University.[2] Subsequently, the bulk of the work on this system has come from the Northwestern group and from a group at the Royal Dutch Shell Laboratories in The Netherlands. Following their initial work, the Selwood group developed a method for the estimation of the nickel particle size distribution in nickel-silica

catalysts from their thermomagnetic curves.[18] This method was an extension of that of Michel,[19] which is based on the assumption that the Curie temperature decreases with decreasing particle size. Using this approach, they studied the relation between the effect of chemisorbed by hydrogen and the particle size distribution. Magnetic measurements were carried out by means of a Faraday balance and by a low field A.C. permeameter.

The Shell Laboratory group has also contributed extensively to this field. Schuit and van Reijen[5] have written an excellent review describing the properties of nickel-silica of different types and different methods of preparation. Broeder,[20] et. al. have studied the effect of hydrogen and other chemisorbed gases on the magnetization of nickel-silica catalysts at fields up to 2000 oersteds using an induction method and on the susceptibility at fields up to 12,000 oersteds using a Gouy balance. Broeder et. al. conclude from their data that the adsorption of one hydrogen atom results in a loss in magnetic moment corresponding to one nickel atom. They have also applied a method developed by Heukelom[21] et. al. to the determination of particle sizes from the magnetization curves. This method is based on the assumption that the individual nickel particles behave as classical paramagnetic entities, an idea which was later verified both experimentally and theoretically by Bean and Jacobs[22] and Becker.[23] They determined activation energies for the sintering process by following magnetically the rate of particle growth at various temperatures.

Dietz and Selwood[24] have recently measured the saturation magnetization of several nickel-silica catalysts and have found that at least for larger particles, the saturation magnetization is within 1% of that of massive ferromagnetic nickel. They have shown by saturation magnetization measurements before and after chemisorption that the magnetization is decreased by 0.6 to 0.8 Bohr magnetons per atom of hydrogen adsorbed. They have also used the magnetization data to estimate particle sizes in several catalysts.

F. OBJECTIVES OF THE PRESENT WORK

The object of the present work was to extend the type of static and low frequency magnetic studies of the nickel-hydrogen system just described to higher frequencies in the radio and microwave range. The reason that the investigation of high frequency magnetic effects might be advantageous for the study of chemisorption is that both are essentially surface phenomena. An applied a.c. magnetic field placed on a sample can penetrate the sample only to a certain depth known as the "skin depth," which is a function of frequency. (More accurately the skin depth is the depth at which the field has decreased to 1/eth of its surface value.) By going to very high (microwave) frequencies one can obtain conditions where the skin depth is only a few hundred atomic diameters. Under these conditions one might expect that any change in

the magnetic structure of the surface brought about by chemisorption would show up as a large effect, whereas at lower frequencies the surface effect would be masked by the much larger effects due to the magnetism of the bulk of the sample. Thus, it might be possible to observe the effect of chemisorbed hydrogen, for instance, on single crystals of nickel, iron, or cobalt where the surface conditions are more accurately known than in the finely divided samples usually studied. In the cases of iron and cobalt the magnetic effect of adsorbed gases has not yet been observed mainly due to difficulty in preparing sufficiently small particles. Gwathmey and Cunningham[25] have shown that the catalytic activity of the different crystal faces of nickel varies markedly. A high frequency magnetic technique might allow a more detailed study of this effect.

In addition to the non-resonant high frequency studies mentioned above, it was thought worthwhile to determine what advantage might be gained by employing magnetic resonance methods to the study of finely divided nickel, particularly with regard to the effects of chemisorbed hydrogen. The most obvious advantage which might be expected from a resonance technique is greatly increased sensitivity, which should allow magnetic studies on very dilute nickel-silica preparations which cannot be conveniently studied by other methods. Preparation of such dilute samples would seem to be one approach to producing very small particles, whose magnetization might be completely quenched by hydrogen adsorption.

A further use of magnetic resonance data on nickel-silica preparations is to verify the data of Bagguley[26] on the g-value and line widths for nickel particles of sub-domain size. Bagguley's results were obtained on particles of uncertain size and under conditions where the degree of contamination of the particle surfaces were also uncertain. The particle size distribution for several of the preparations used in this work have been estimated by the magnetic method and have been found to be considerably less than a skin depth for the approximately 9.5 KMc/sec. microwaves used in the resonance experiments, this being a requirement for the application in its simplest form of the theory of ferromagnetic resonance developed by Kittel,[27] Polder[28] and Van Vleck.[29]

It has been suggested by Dietz[30] that a measurement of the g-value of nickel before and again after chemisorption has occurred would allow some conclusions to be drawn about the mechanism by which the magnetism of the nickel is decreased. Therefore, it was considered desirable to determine the effect of adsorbed hydrogen on the g-value of nickel.

These, then, are the points which have provided impetus for this research.

IV. MAGNETIC PROPERTIES OF FINELY DIVIDED NICKEL

Before proceeding to the discussion of the experimental procedures and results obtained from the high frequency magnetic studies of disperse nickel-silica systems, it seems desirable to review briefly the magnetic classification of matter and to describe the type of magnetic behavior which finely divided ferromagnetic materials have been found to exhibit.

Materials may be classified magnetically as diamagnetic, paramagnetic, or ferromagnetic. This classification is based on the behavior of various materials in the presence of an inhomogeneous magnetic field. Diamagnetics have a slight tendency to move toward regions of weaker magnetic fields; paramagnetics have a slight tendency to move toward stronger fields; ferromagnetics are drawn strongly toward stronger fields.

Diamagnetism arises from the induction according to Lenz' Law of microscopic orbital currents in the molecules of a substance by an applied magnetic field. The induced current produces a field in opposite direction to the inducing field and thus results in repulsion of the substance by the field.

Paramagnetics have a permanent magnetic moment due to unpaired electron spins. When such substances are placed in a magnetic field their unpaired spins tend to align in the direction of the applied

field. This tendency to align is opposed by thermal agitation. The balance between those opposing forces is expressed by the Langevin equation:

$$\frac{I}{Io} = \coth \frac{\mu H}{kT} - \frac{kT}{\mu H} \qquad (1)$$

Here I = intensity of magnetization at H and T

Io = saturation magnetization

H = applied magnetic field

T = absolute temperature

k = Boltzmann constant

μ = magnetic moment

This equation is derived by application of the Boltzmann distribution law to an assembly of non-interacting paramagnetic entities and hence it involves the assumption that the entities are in thermal equilibrium with the field and their surroundings.

Ferromagnetics are similar to paramagnetics in possessing permanent magnetic moments which are able to align in an external field. They differ, however, in that the individual moments interact strongly giving rise to regions called "Weiss domains" in which all of the individual moments have the same orientation. Prior to the application of an external magnetic field, the domains are oriented at random giving rise to no net magnetization. When an external field is applied the individual domains turn into alignment with the field giving rise to a

large magnetization, which persists to a greater or lesser degree after removal of the applied field.

There are two important mechanisms by which the domains become oriented in the applied field: 1) by domain wall motion in which a favorably oriented domain grows at the expense of ones less favorably oriented, 2) by a coherent rotation of the atomic moments making up the domain.

The ferromagnetic properties of a given substance disappear above a certain critical temperature, known as the "Curie temperature" and the substance then behaves paramagnetically. The Curie temperature then corresponds to the point at which the thermal energy, kT, is just sufficient to overcome the interatomic forces giving rise to domains. These so-called "exchange forces," it should be mentioned, are explicable only in terms of quantum mechanics, are of Coulombic origin and have no classical analogue.

The magnetic behavior of the finely divided nickel-silica preparations of interest here falls into an intermediate classification named "superparamagnetism" by Bean.[31] A complete review of the subject of superparamagnetism is given by Bean and Livingston,[32] to which the reader is referred for a more authoritative account than the brief one to be given here.

The process of dividing a ferromagnetic substance into domains will continue until the energy due to the forces favoring such a process

is equal to that of the forces opposing it. As mentioned above, the exchange forces favor parallel alignment of all of the magnetic moments of a ferromagnetic substance, while the magnetic forces favor an alignment which avoids the formation of magnetic poles. The upper limit for single domain size, if the domain is assumed spherical, is a diameter of about 300 Å. Any ferromagnetic particle whose diameter is much less than this will then consist of a single domain. Although a multidomain particle can magnetize by both domain wall motion and coherent rotation of atomic moments, a single domain particle is constrained to magnetize only by rotation. Such a particle may be thought of as a paramagnetic atom of very large, effectively infinite, spin quantum number, and the magnetization of an assembly of such particles can be expected to obey the classical equation of Langevin:

$$\frac{I}{Io} = \coth \frac{\mu H}{kT} - \frac{kT}{\mu H} \qquad (1)$$

The meanings of the symbols in this equation are identical with those given on page (13) except that now μ is the magnetic moment of a polyatomic particle rather than the atomic moment. Thus, $\mu = n\mu_n$, where n is the number of atoms in the particle and μ_n is the magnetic moment per atom. It must be borne in mind that in the derivation of the equation, it is assumed that the particles are in the thermal equilibrium with the lattice and that the particles do not interact among themselves. The connection between the magnetization and particle size is shown by the equation, $\mu = \mu_n n$. If I, Io, H and T

are measured μ can be determined. From μ and μ_n, the known atomic moment, n, and therefore the particle size, can be determined.

Since real particles never exhibit completely isotropic magnetic behavior, energy barriers arising from the anisotropy energy will occur. At any temperature where kT is less than the anisotropy energy, thermal equilibrium may not obtain and the Langevin equation may not apply. In general, smaller particles will obey the equation better than larger ones and a given set of anisotropic particles will obey more closely the higher the temperature. If a range of particle sizes is present, the magnetization behavior will be the sum of the contributions from all the particles.

V. MAGNETO-ABSORPTION

By magneto-absorption is meant here the absorption of energy from an alternating magnetic field caused by the presence of magnetic material. This definition will include both resonant and non-resonant absorption.

If a sample of a magnetic material is placed in an alternating magnetic field, removal of energy by the field can be expected to take place by a number of possible mechanisms. Important among these are 1) hysteresis losses, 2) ohmic or resistive losses due to eddy currents induced in the sample, and 3) losses which are accountable to the gyromagnetic properties of magnetic materials and are resonant in nature. Although all magnetic materials will show some losses in an alternating field, the mechanism responsible for these losses will vary depending on the constitution of the sample and with the frequency. For example, in non-metallic ferrites it would be expected that mechanisms 1) and 3) should be the principal contributors, since the electrical conductivity of such materials is virtually nil. On the other hand, in non-ferromagnetic metallic substances, it is probable that mechanism 2) would be the chief contributor. For a magnetic metal such as iron all three mechanisms can be expected to make considerable contributions to the total losses.

The absorption of energy just discussed is not the only effect which a magnetic sample can have on an alternating magnetic field in which it is placed. In addition, the sample may change the frequency of the field, a phenomenon known as dispersion. In real systems absorption and dispersion always occur together and the two are not independent but are connected by the Kronig-Kramers[33] relations. In order to treat the overall interaction of a magnetic sample and an alternating field mathematically, the complex magnetic susceptibility, $x = x' - ix''$, is formally introduced.[34] The real part of the complex susceptibility gives rise to a magnetization in phase with the magnetic field, while the imaginary part gives rise to an out-of-phase component. The in-phase component is associated with the dispersion while the out-of-phase component corresponds to absorption. From a slightly different point of view, x' corresponds to a change in the inductance of a coil supplying the alternating field, while x'' corresponds to a change in the effective resistance of the coil, regarded as a lumped circuit element. A change in the resistive component of the susceptibility will be reflected as a change in the quality factor, Q, of the coil. At a given frequency and constant coil inductance the change in Q will be a direct measure of the resistive (or imaginary) component of the susceptibility.

In a practical circuit, of course, the effect of the reactive (or real) part of the susceptibility on the coil Q must be

taken into account. This effect can be minimized, however, by keeping the coil filling factor small.

The relationship between the radio-frequency losses and the sample induction for a high permeability alloy is shown in Figure 1, which was kindly furnished by W. Earl Bell of Varian Associates. The magnetoabsorption ordinate $\frac{\Delta Q}{Q}$ shows the small contribution of the reactive component to the observed Q. The filling factor here was about 1%. Despite such small filling factors, the losses due to the out-of-phase component can be observed with great amplification when the sample is the core of a coil excited by a linear oscillator. In the limit such an oscillator is infinitely sensitive to Q changes since the feedback loop gain is unity; in practice, however, sufficient non-linearity is present to stabilize the operating level and allow observations of Q changes to about 1 part in 10^6.

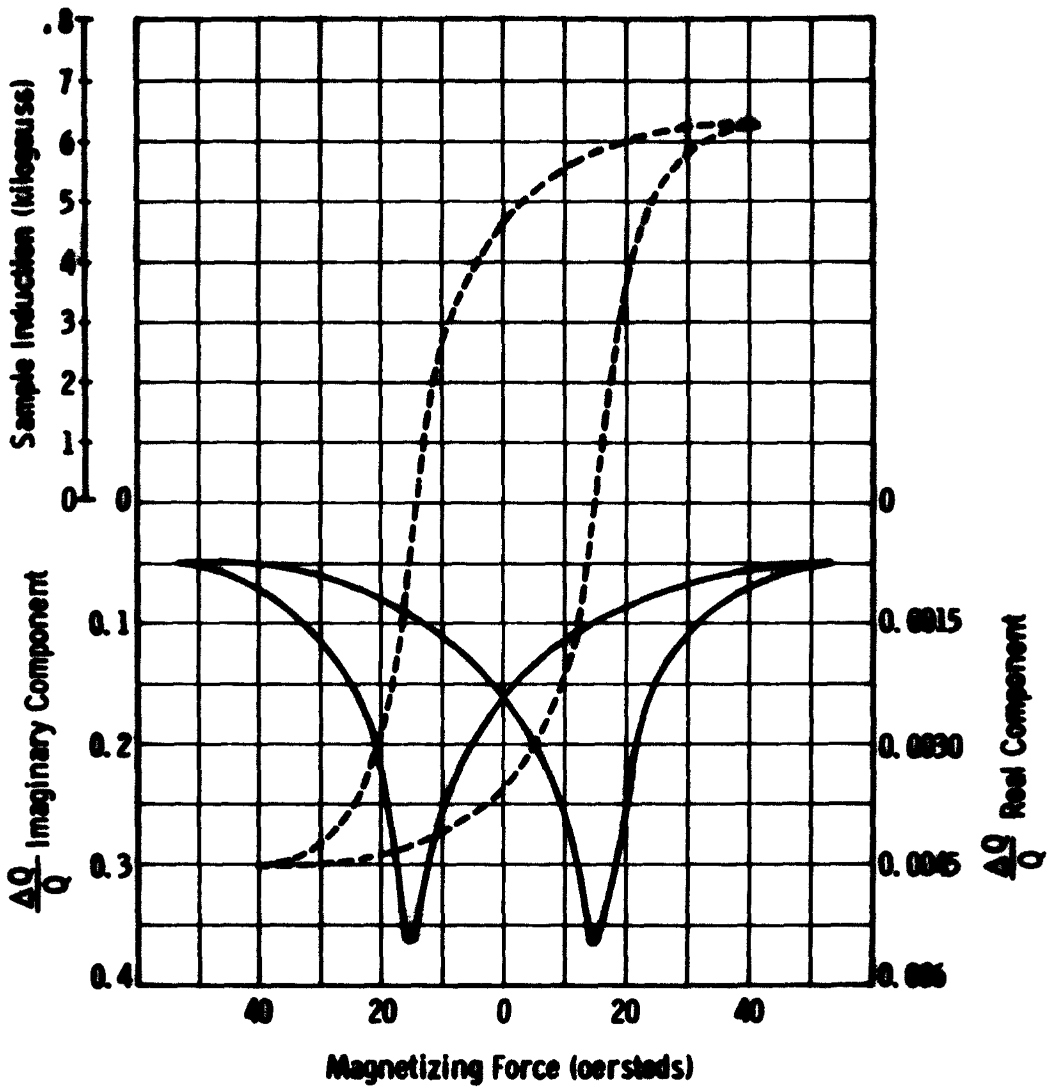


FIGURE 1
RELATIONSHIP BETWEEN THE CORE SAMPLE INDUCTION (DOTTED LINE) AND THE R.F. MAGNETOABSORPTION (SOLID LINE) FOR A HIGH PERMEABILITY MATERIAL. THE COIL FILLING FACTOR IS ABOUT 1% AND RELATIVELY LARGE MAGNETIZING FORCES ARE REQUIRED TO SATURATE THESE SHORT SPECIMENS

VI. FERROMAGNETIC RESONANCE

Since a good proportion of the experimental work to follow involves the ferromagnetic resonance of nickel particles, it seems desirable here to discuss mechanism 3) of the previous paragraph in more detail.

Paramagnetic and ferromagnetic materials owe their magnetic properties to the existence of unpaired electrons in the atoms of which they are composed. Associated with the intrinsic spin angular momentum of the electron is a magnetic moment. In the presence of an applied magnetic field the spinning electron will experience a torque tending to align it with the field. As a result of this torque, the angular mementum vector will precess about the direction of the applied field. If the precessing magnetic moment is now subjected to a rotating magnetic field at the precession frequency a resonant absorption of energy from the field will result. In the case of ferromagnetics, it is more convenient to consider that the macroscopic magnetic moment, made by summing the individual atomic moments, precesses about the applied field. For a general ellipsoid with demagnetizing factors N_x, N_y, N_z the condition for ferromagnetic resonance as first shown by Kittel[35] is:

$$h\nu = g\beta\left\{\left[H_z + \left(N_x - N_z\right) M_z\right]\left[H_z + \left(N_y - N_z\right) M_z\right]\right\}^{1/2} \tag{2}$$

Here h = Planck's constant, ν = frequency, g = spectroscopic splitting factor, β = Bohr magneton, H_z = applied magnetic field, and M_z = magnetization in z direction. In the derivation of this equation effects of magnetic anisotropy are neglected. The g-values obtained experimentally using this equation are generally near the free electron value of 2, and for fields of a few thousand oersteds, the resonant frequency is in the microwave range. For a spherical sample, where $N_x = N_y = N_z$, equation (2) simplifies to

$$h\nu = g\,\beta H_z\,, \tag{3}$$

which is identical with the equation for ordinary paramagnetic resonance.

VII. MAGNETIC LOSSES AT 3.7 AND 13 MC/SEC

A. EXPERIMENTAL

1. PREPARATION OF SAMPLES

A variety of recipes is available for the preparation of finely divided nickel-silica systems. (See Reference 5.) These involve two main methods for introducing the metal into the silica support, impregnation and coprecipitation.

In the impregnation method an aqueous solution of a nickel salt, usually the nitrate is mixed with a slurry of silica gel and the resulting mixture is dried, and finally reduced in hydrogen at elevated temperature to produce small metal particles separated by the relatively inert silica matrix.

In the coprecipitation method, hot solution of nickel nitrate and sodium meta-silicate are mixed to produce a gel-like precipitate of what may be regarded as nickelous hydro-silicate, according to the reaction:

$$Ni(OH)_2 + Si(OH)_4 \rightarrow NiOSi(OH)_3 \qquad (4)$$

The samples used in this study were prepared by both methods. For samples of low nickel content it was necessary to add

nitric acid to the nickel nitrate solution in order to cause co-precipitation when the boiling nickel nitrate and sodium silicate solutions were mixed. Impregnation catalysts were prepared by mixing Davison silica gel with a nickel nitrate solution of the desired concentration. The sodium meta-silicate and nickel nitrate were Baker's Reagent grade chemicals.

In addition to the samples especially prepared, many experiments were carried out using a commerical catalyst manufactured by the Universal Oil Products Company and hereinafter designated U.O.P. This sample is an impregnation type nickel-on-kieselguhr (a diatomaceous earth) preparation which has been studied considerably by other workers.[36] Some experiments were also done using an impregnation catalyst containing about 10% nickel which was kindly furnished by Mr. Ivan den Besten of Northwestern University.

2. ANALYSIS OF SAMPLES

All samples were analyzed for nickel by a standard electrodeposition technique. Samples were dissolved in hydrofluoric acid and a few drops of sulfuric acid were added. The solution was then evaporated to fumes of SO_3, then taken up with water and nitric acid. The nickel was then electrodeposited on weighed platinum electrodes.

The samples used in this study are listed by Roman numerals in Table I with their nickel analysis, and method of preparation.

TABLE I
ANALYSIS OF $NI\text{-}SIO_2$ PREPARATIONS

Sample Number	Method of Preparation	% Nickel
I	U.O.P.	46.9
II	Impregnation	9.8
III	Coprecipitation	4.2
IV	Impregnation	1.1
V	Coprecipitation	0.98

3. NON-RESONANT LOSS MEASUREMENTS AT 3.7 AND 13.0 Mc/sec

In order to determine the feasibility of using radio-frequency loss measurements as a means of studying the magnetic effect of chemisorbed hydrogen on finely divided nickel experiments were carried out in which a sample of reduced U.O.P. catalyst was made the core of a radio-frequency coil excited by a linear oscillator. The observation of the effect, on the oscillator output, of incremental additions of hydrogen to the catalyst was made possible by a vacuum system and an associated volumetric pipette system.

a. Vacuum and Volumetric Pipette Systems

A schematic diagram of the vacuum and volumetric pipette systems is shown in Figure 2. Figure 3 is a photograph of the same apparatus. The system consists of two main parts:

LEGEND:

A - Hydrogen Tank and Deoxo Unit
B - Helium Tank
C - Safety Manometer
D - Tube Heater Packed with Cu on Asbestos
E - Silica Gel Trap
G - Helium Storage Bulb
H - Hydrogen Storage Bulb
I - Standard Volume
J - U-Tube Manometer
K - U-Tube Manometer
L - Gas Pipette
M - Sample Chamber
N - Sleeve Heater
O - Cold Trap
P - Oil Pump
R - Vacion® High Vacuum Pump
S - To Atmosphere
T - Exhaust
U - R-F Coil
1 through 18 - Stopcocks

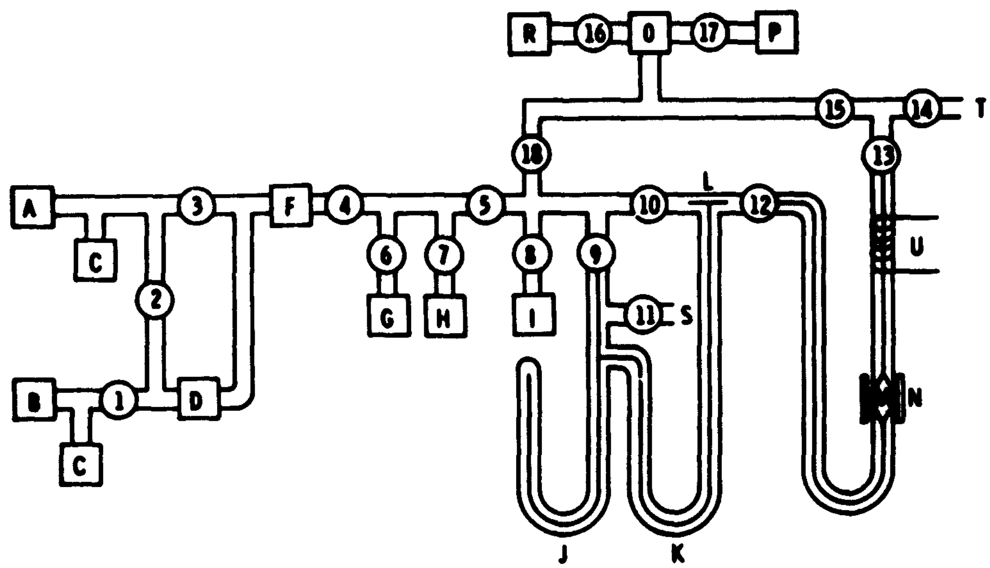


FIGURE 2
SCHEMATIC DIAGRAM OF THE VACUUM AND VOLUMETRIC PIPETTE SYSTEMS

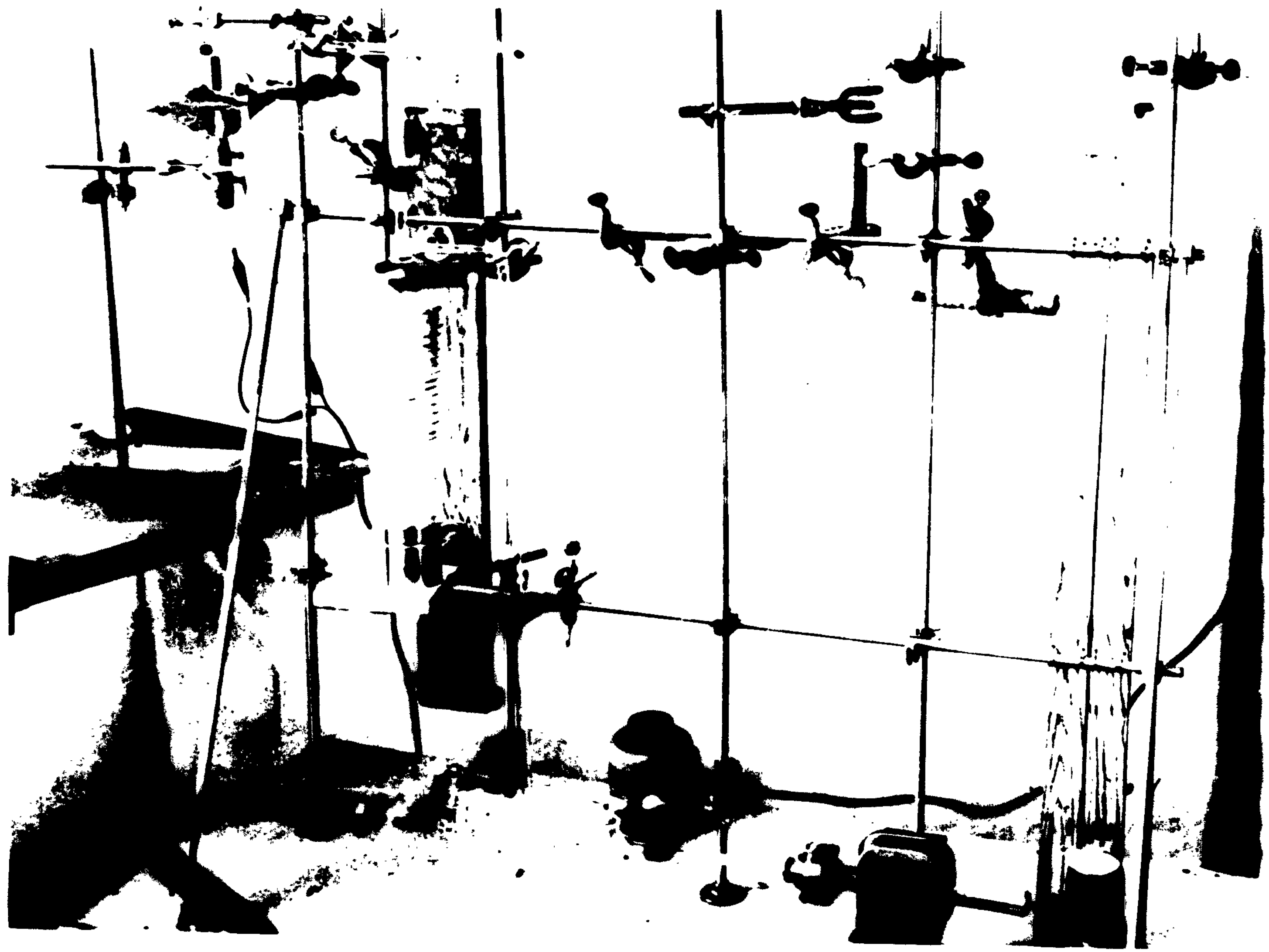


FIGURE 3

PHOTOGRAPH OF THE VACUUM AND VOLUMETRIC PIPETTE SYSTEM

(1) Purification trains for hydrogen and helium

(2) The volumetric adsorption system

The helium, which is used in measuring the volumes of the various parts of the adsorption apparatus is freed of oxygen by passage through the heated tube D (Figure 2) which is packed with copper-on-asbestos. The gas is then passed through the liquid nitrogen-cooled silica gel trap F, and into the storage bulb G, where it is kept for later use. The helium used was taken from a commercial tank. Electrolytic grade hydrogen is purified for use by passage through a Deoxo catalytic purification unit (Baker Chemical Company) attached to the tank outlet and through the cold silica gel trap F, and is then stored in the bulb H.

The volumetric adsorption apparatus consists of the gas pipette L, the closed-ended U-tube manometer J, and the U-tube manometer K, which was constructed of one millimeter inside diameter Pyrex capillary tubing in order to decrease the dead space in the gas pipette. The sample, placed in the chamber M, can be surrounded by the sleeve furnace N in order to heat it to a suitable temperature for reduction. The furnace can then be removed and replaced by the radio-frequency coil U for the loss measurements.

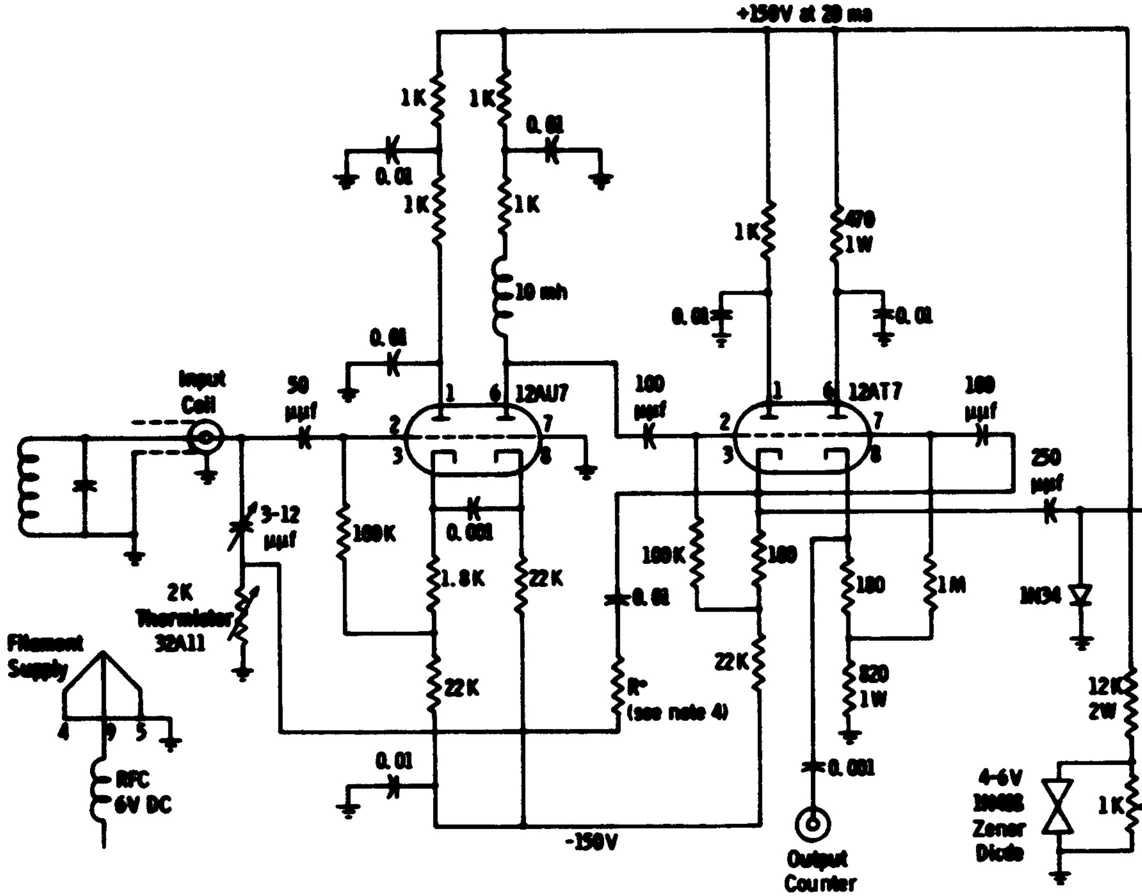
b. Linear Oscillator

As mentioned in an earlier section, a magnetic material introduced into a coil carrying a radio-frequency current will cause a

change in the quality factor, Q, of the coil. The coil Q is defined as $\frac{\omega L}{R}$ where ω is the frequency, L, the coil inductance and R, the effective coil resistance. R represents any losses occurring in the coil whether ohmic in nature or not. An equivalent definition of Q is that it is the ratio of the energy stored to that lost by the coil per cycle.

In this work a linear oscillator was used to detect changes in the Q of a coil caused by magnetic changes in a sample forming the cone of the coil. A schematic diagram of the oscillator circuit used is shown in Figure 4. The frequency of oscillation was determined by the coil used. The coil was connected to the oscillator by means of a BNC connector, so that the frequency could be changed quite easily. The level of oscillation of an oscillator such as this is extremely sensitive to changes in the Q of the coil which it drives. Similar oscillators can be made to detect Q changes of as little as one part in 10^6. A discussion of oscillators of this basic type and consideration of their design is given by Robinson.[37]

The oscillator current was rectified by a Zener diode and was monitored by a Varian G-10 recorder. The sensing coils were wound on plastic cylinders one inch in diameter and about three inches in length. In order to prevent stray pick-up, the coils were inclosed in copper boxes. As shown in Figure 4, the oscillator was provided with an output plug for connection to a frequency counter. This was necessary to insure that it was actually changes in the resistive



NOTE:

1. All capacitor values are in μf unless otherwise noted.
2. All resistance values are in ohms unless otherwise noted.
3. Use chokes on all heaters and stable d-c supplies.
4. Resistance chosen to set r-f level 1V rms across tank.

FIGURE 4
SCHEMATIC DIAGRAM OF LINEAR OSCILLATOR CIRCUIT

component of the circuit Q which were being observed rather than output changes due to a large frequency shift. The observed frequency shifts on saturating the nickel sample with hydrogen were only about .1% for the approximately 1% filling factor used.

c. **Experimental Procedure**

A typical experiment was carried out as follows:

A weighed sample of the U.O.P. nickel catalyst was sealed into the sample chamber M (Figure 2) of the vacuum system. The sample was in the form of cylindrical pellets somewhat less than three millimeters in diameter by about three millimeters long. Several pellets stacked in a three millimeter inside diameter pyrex tube formed the sample. The sample was surrounded by a small quartz tube furnace wound with resistance wire. Hydrogen from the tank A was then allowed to flow slowly over the sample and was exhausted from the system through stopcock 14. Voltage was then applied to the heater, N, sufficient to raise the sample temperature to about 350°C as measured by a thermocouple affixed to the sample tube. The hydrogen treatment was usually continued for at least twelve hours to insure complete reduction. After the reduction treatment, the sample was pumped to a pressure of less than 10^{-6} mm Hg while the temperature remained at 350°C. Two to four hours of pumping using a Varian VacIon® pump was usually required to reach this pressure.

When the sample had been reduced and evacuated, the sleeve furnace was removed and replaced by the radio-frequency coil. The coil was clamped firmly in place and then the change in the output level of the linear oscillator was noted. Known amounts of hydrogen were then admitted to the sample and the change in oscillator output for each sample was noted. From the known volumes of the various parts of the vacuum system and the measured pressures before and after admission of hydrogen the amount of hydrogen actually adsorbed by the sample could be computed. It was necessary to wait a short time after admission of the hydrogen for the system to return to thermal equilibrium. This is because the heat of chemisorption ($\sim$ 30 K cal. mole, initially) raises the temperature of the nickel thus lowering its magnetization in excess of the lowering due to the chemisorption bond alone. This transient thermal effect is also observed in static field measurements and has been used by Selwood[38] to estimate the heat of chemisorption of hydrogen on nickel.

B. RESULTS AND DISCUSSION

In Figures 5 and 6 are shown the fractional change in oscillator output plotted against the volume of hydrogen adsorbed per gram of nickel in the sample. Figure 5 gives data obtained using a 3.71 megacycle oscillator while Figure 6 gives the results at 13.0 megacycles.

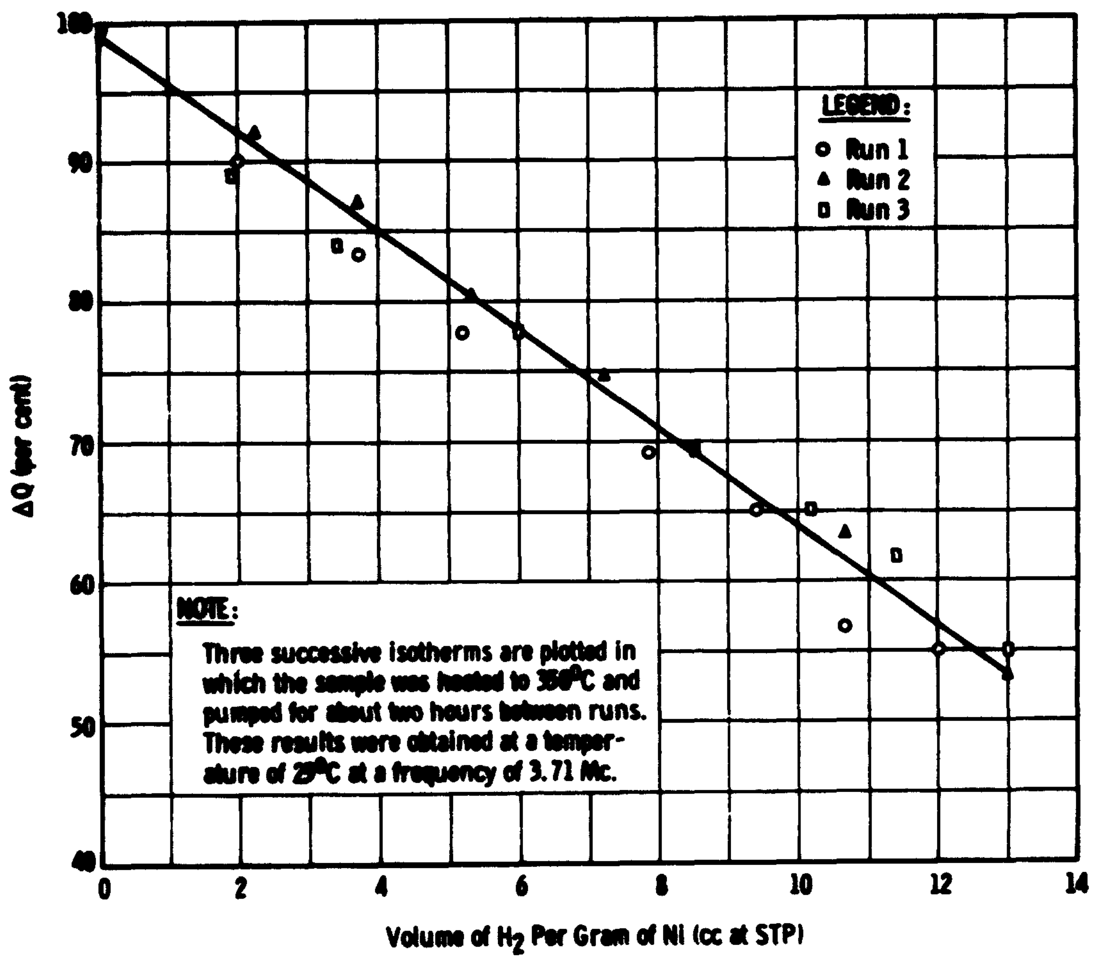


FIGURE 5

ΔQ, THE FRACTIONAL CHANGE IN OSCILLATOR OUTPUT VS THE VOLUME OF HYDROGEN PER GRAM OF NICKEL AT STANDARD TEMPERATURE AND PRESSURE FOR A NICKEL-ON-KIESELGUHR CATALYST (U. O. P.), FREQUENCY = 3.71 Mc

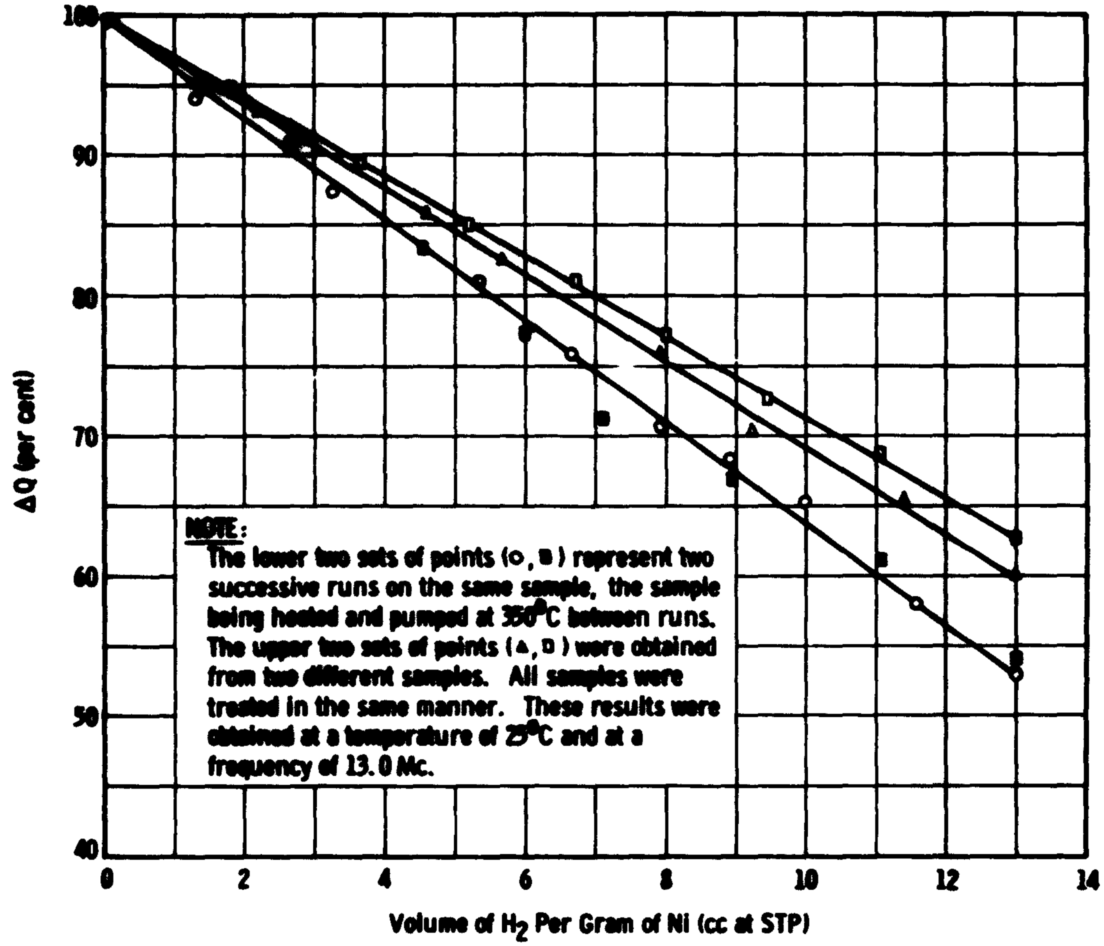


FIGURE 6

ΔQ, THE FRACTIONAL CHANGE IN OSCILLATOR OUTPUT VS THE VOLUME OF HYDROGEN ADSORBED PER GRAM OF NICKEL AT STANDARD TEMPERATURE AND PRESSURE FOR A NICKEL-ON-KIESELGUHR CATALYST (U.O.P.), FREQUENCY = 13.0 Mc

Here the ordinate, ΔQ, was obtained as follows: The oscillator was allowed to warm up until its output became stable. The sample was then inserted into the coil and the difference in oscillator output ΔE_s was noted. A measured amount of hydrogen was then admitted, causing an increase in oscillator output, ΔE_H. The fraction of the original effect remaining after each hydrogen addition is then $\Delta Q = \frac{\Delta E_s - \Delta E_H}{\Delta E_s}$. Note that the effect of hydrogen addition is an increase in the coil, Q, corresponding to the effect of removing a part of the sample from the coil.

In order to establish that the results obtained were actually of magnetic origin, a finely divided platinum on alumina catalyst containing approximately the same amount of metal as the nickel catalysts was used in place of the nickel. Platinum has conduction properties similar to nickel but is not ferromagnetic. The insertion of the platinum sample had little effect on the oscillator output and no difference was observed when hydrogen was admitted.

These results are in broad agreement with those obtained by static and low-frequency fields by other workers,[38, 39] and they can be given substantially the same interpretation. If we assume that the measured changes in oscillator output reflect changes in the magnetic losses of the sample and hence changes in sample magnetization, then the linearity of the ΔQ versus V_{H_2} isotherms indicates a linear change in magnetization with the volume of hydrogen adsorbed. The interpretation accorded this effect is that the adsorbed hydrogen atoms

contribute electrons to the unfilled d-band of the nickel. Since the unpaired d-electrons are thought to be responsible for the observed ferromagnetism of nickel, the filling of the d-band results in a decrease in the magnetic moment of the nickel and consequently decreases the magnetization. The saturation magneton number for ferromagnetic nickel as determined from measurements at high field and low temperatures is 0.6 Bohr magnetons, and recent results by Dietz and Selwood[24] indicate that approximately .6 - .8 Bohr magnetons of magnetic moment are lost per atom of hydrogen adsorbed.

The principal feature in which the high frequency results differ from those obtained in static and low frequency fields is the greater fractional change observed when the sample is saturated with hydrogen. The total fractional change in magnetization found at high frequencies is more than thrice the effect found in static and low frequency fields.

To summarize the various types of measurements which have been applied to the U.O.P. preparation Table II is presented.

TABLE II

FRACTIONAL CHANGE IN MAGNETIZATION FOR U.O.P. SAMPLE AT SEVERAL FREQUENCIES

Method	Frequency of Measurement	Quantity Measured	% Change on H_2 Adsorption	Reference
Saturation	Static	$\frac{\Delta M_s}{M_s}$	6	37
Low-field Permeameter	60 cps	$\frac{\Delta M}{M}$	13	38
3.7 Mc Oscillator	3.7 Mc/sec	$\frac{\Delta Q}{Q}$	46	Present Work
13.0 Mc Oscillator	13 Mc/sec	$\frac{\Delta Q}{Q}$	41	Present Work
Magnetic Resonance	Equivalent to Static Method	$\frac{\Delta A}{A}$	6	Present Work

In the column, "Quantity Measured," M_s is the saturation magnetization, M is the magnetization at non-saturation condition, Q is the quality factor of the linear oscillator coil, A is the intensity of magnetic resonance absorption, while ΔM_s, ΔM, ΔQ and ΔA are the changes in these quantities on saturation with hydrogen. Although the fractional change in saturation magnetization under a static field condition is only about one-half the change in magnetization found in low field permeameter experiments, a frequency effect is not involved here, since Dietz[30] has shown that the relative magnetization change at low

field should be at least a factor of two greater than the change in saturation magnetization. The coil Q is a measure of the losses occurring in the coil and since the losses in these samples appear to be primarily magnetic, it is assumed intuitively that Q is proportional to M.

The increased sensitivity to adsorbed hydrogen at radio frequencies can be understood in a semi-quantitative way through consideration of the superparamagnetic properties of the catalyst and the relaxation behavior to be expected from small particles. Owing to its larger surface to volume ratio, a small particle will suffer a greater fractional loss in magnetic moment on monolayer adsorption of hydrogen than a larger one. However, according to the Langevin equation, in a sample containing a distribution of particle sizes, the larger particles will contribute a larger share of the total magnetization than the smaller ones due to their larger magnetic moment and consequent diminished influence of thermal fluctuations. Thus, in static or low frequency fields, the total effect observed on chemisorption of hydrogen to saturation will be the sum of the effects due to all the particles in the sample.

If the frequency at which the magnetization changes are measured is increased, however, relaxation effects may come into play and some particles may be effectively left out of the magnetic measurement simply because they are unable to follow the magnetizing field.

Neel[40] has shown that the approach to equilibrium of an assembly of initially aligned uniaxial particles proceeds accoring to the formula

$$M_r = M_s \exp(-t/\tau) \qquad (5)$$

where

$$1/\tau = f_o \exp(-KV/KT) \qquad (6)$$

Here M_r is the remanent magnetization, M_s the saturation magnetization, t the time, and τ the relaxation time characteristic of the exponential decay, f_o is a frequency factor of the order of 10^9 sec^{-1}, K is the anisotropy energy per unit volume, V is the volume of the particle, and K is the Boltzmann constant. Since as shown by equation (6), the relaxation time is a positive exponential function of the volume, there will be a certain volume at which the relaxation time will become very long with respect to the time required for measurement, while smaller particles will come to equilibrium almost instantly.

For the case of anisotropy of cubic symmetry, as would be the case for spherical nickel particles with normal magnetocrystalline anisotropy, the energy barrier to rotation from the easy 111 direction through the medium 110 direction is $\frac{K_1V}{12}$ where K_1 is the first order magnetocrystalline anisotropy constant. Using the value given for K_1 for nickel in Bozorth's monograph:[41] $K_1 = 5.0 \times 10^4$ $ergs/cm^3$ (300^oK), the particle radius corresponding to any particular relaxation time

can be calculated. If we calculate the particle size for a relaxation time $\tau = 1/\nu$, where ν is the frequency of the measuring field, the result will be, roughly speaking, the size of the largest particle which can follow the field variation. Particles much larger than this size will be unable to contribute to the magnetic losses in the sample. At 300°K, the particle radius corresponding to a frequency of 10 Mc/sec, and hence, a relaxation time of 10^{-7} sec. is 43 Å, while at a frequency of 100 cps the radius is 159 Å. Thus, the high frequency results measure contributions from particles with radii of about 43 Å and smaller, while the low frequency results include contributions from particles of about 159 Å or less. Due to the larger surface to volume ratio of the smaller particles we expect to find a greater fractional decrease in the magnetization on hydrogen chemisorption at higher frequencies than at lower ones, as is found experimentally. This effect may not be observed if the smaller particles are less accessible to hydrogen than the larger, as apparently sometimes occurs.

If the interpretation of the increased sensitivity to hydrogen at radio frequencies is correct, it would seem to offer a method for obtaining a sort of spectrum of the particle sizes present in a disperse preparation by changing the temperature over a range while observing the radio-frequency losses at a fixed frequency, since according to equation (6), only particles of a certain maximum size can contribute to the magnetic losses at a given frequency and temperature.

Application of this method might shed light on the so-called "slow" or "activated" adsorption of hydrogen on disperse nickel, a process which is thought to be concerned especially with smaller particles. Since the use of a sufficiently high frequency would "sort out" the smaller particles from the larger ones, any effect peculiar to the small particles would be amplified.

The magnetic resonance results, which will be discussed later, are included here for completeness. Although the resonant frequency is 9.5 KMc/sec., the absorption signal obtained is proportional to the magnetization of the sample. Hence, the resonance results are equivalent to a static field magnetization measurement.

VIII. ATTEMPT TO DETECT THE EFFECT OF HYDROGEN ON BULK METALS AT 9.5 KMC

Several experiments were undertaken in the hope of detecting the effect of hydrogen chemisorption on the surface magnetic properties of bulk ferromagnetic metals. It was hoped that the small skin depth of these metals for microwaves would make the microwave losses sensitive to surface effects. If this were true, it should be possible to study the effects of chemisorbed gases on selected crystal faces of single crystals of transition metals. It would also be useful to show that hydrogen produces a magnetic effect on cobalt and iron as well as nickel. Thus far it has not been possible to show this effect on iron and cobalt due to the difficulty of preparing sufficiently small particles.

Although the results of these experiments have been disappointing, it is probably worthwhile to describe the experimental procedures followed and to discuss the possible reasons for our failure to obtain a clear effect.

In the experimental procedure, the metal sample was sealed into a cell made of 11 mm quartz tubing and was held in place by two quartz coil springs which permitted thermal expansion of the metal during heat treatment but held the sample firmly in position. Each end of the quartz tube was fitted with a quartz-to-pyrex graded seal

to allow attachment of the cell to the vacuum system and to a small reservoir of hydrogen gas which could later be admitted to the metal through a beak seal. A diagram of the sample cell is shown in Figure 7.

The sample tube was then sealed to the simple vacuum system shown schematically in Figure 8. Two liquid nitrogen traps were interposed between the sample and the stopcocks leading to the hydrogen inlet and the pumps, respectively, to avoid adsorption of stopcock grease on the sample. A Deoxo purifier was interposed between the nitrogen trap and the hydrogen supply to remove oxygen from the electrolytic grade hydrogen used.

After the system had been flushed several times with hydrogen, the sample tube was filled with hydrogen to a pressure of about one atmosphere, and the sample was heated at 550-600°C for several hours by means of a sleeve resistance heater. In this hydrogen heat treatment no effort was made to remove water from the hydrogen before use.

The system was then pumped down with the rough pump and the two traps immersed in liquid nitrogen. The system was pumped further using a VacIon® pump, the sample remaining at 550-600°C. After pumping for about 12 hours, the pressure, as determined from the calibration of the VacIon pump current, was between 10^{-9} and 10^{-8} mm Hg. About 50 microns of purified helium was then admitted and the sample tube was flame sealed from the vacuum line. The hydrogen reservoir was filled

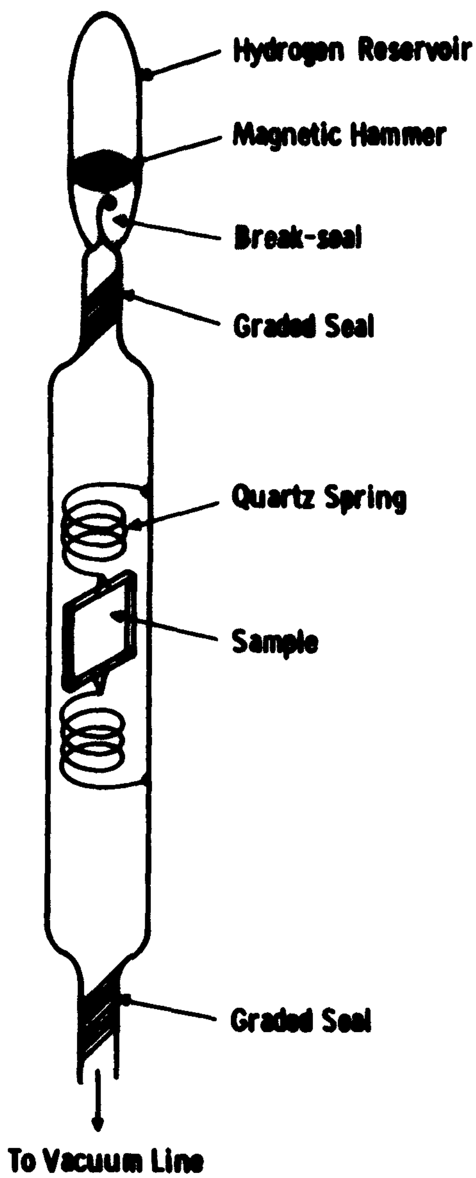


FIGURE 7
SAMPLE TUBE FOR BULK METAL SAMPLES

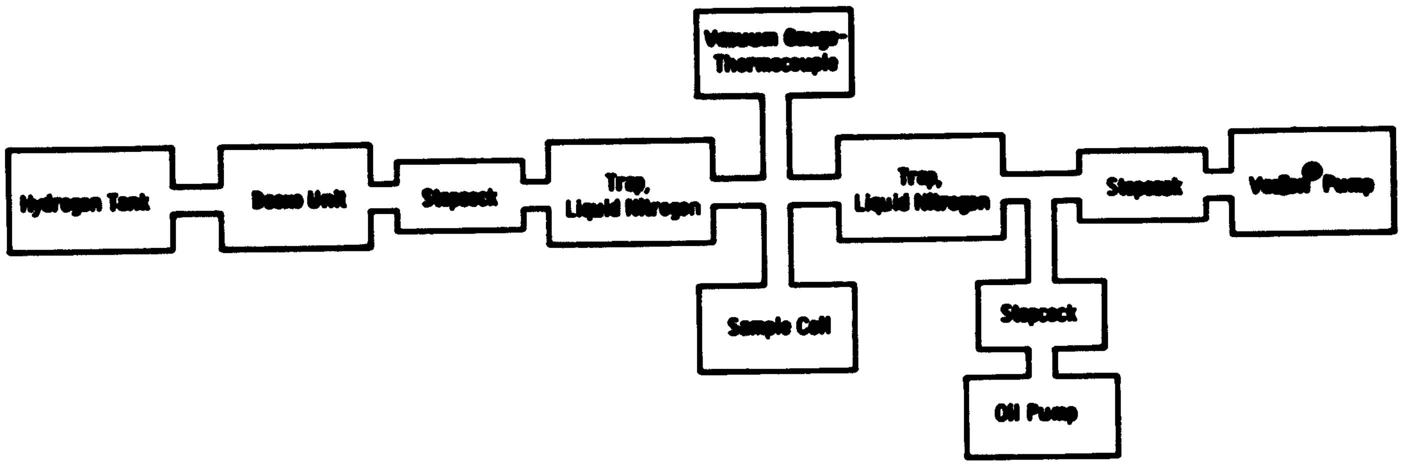


FIGURE 8
VACUUM SYSTEM USED FOR BULK METAL SAMPLES

by sealing the opposite end of the sample tube to the vacuum system. After flushing and degassing the system, about 1000 microns pressure of hydrogen was admitted to the reservoir which was then fire sealed from the vacuum line. The hydrogen was passed through the Deoxo purifier and the liquid nitrogen trap before entering the reservoir.

The prepared sample was then placed in a microwave cavity which was resonant at approximately 9.5 KMc. To minimize electrical losses, the flat, rectangular-shaped sample was oriented so that the faces of the rectangle were perpendicular to the electric part of the microwave field and parallel to the magnetic microwave field. The cavity formed one arm of the microwave bridge in a standard Varian V-4500 EPR spectrometer with 100 kc field modulation. Any change in the modulated microwave power reflected from the cavity was phase-detected at 100 kc and monitored by a Varian G-10 graphic recorder Any field dependent change in the cavity Q would thus be reflected as a deflection of the recorder

The extent of any effect observed on hydrogen adsorption might be expected to be affected by any d-c bias field applied to the sample, and by the previous magnetic history of the sample. Ferromagnetic samples show a very broad resonant microwave absorption, which in the case of the iron and nickel samples used in these experiments extended down to zero applied field due to remanence in the sample. Most of the experiments were done in the absence of a d-c field, although in some cases the sample had been previously

magnetized. The 100-kc modulation may be regarded as sampling the slope of the ferromagnetic resonance curve for the sample and producing d-c signal proportional to this slope. An effect can then be observed if the adsorption of hydrogen causes sufficient change in the slope of the ferromagnetic resonance curve.

This experiment was carried out on various samples of bulk nickel and on one sample of pure iron. The nickel samples included a single crystal of nickel cut along the 100 plane, and nickel shim stock of various grades. In addition, the experiment was performed using a sample of platinum foil to compare any effect on the magnetic metals with that on a non-magnetic one

The results of this type of experiment proved notably non-reproducible. Both the iron and nickel samples sometimes showed a small effect when hydrogen was admitted and sometimes no effect at all. In no case did the platinum show any effect. The recorder deflections were always in a direction corresponding to an increase in cavity Q when hydrogen was admitted. Thus, in spite of their inconclusive nature, these results do suggest that a real effect is being observed and that it is due to a magnetic change rather than an electrical one. The non-reproducibility of the data may be due to variations in the degree of cleanliness of the sample. The sealing off of the sample tube from the vacuum line, for instance, might drive varying amounts of gas into the sample chamber, thus saturating the metal surface in some instances. It would be preferable for this

experiment to build the sample preparation system directly into the microwave apparatus in a permanent way. This, however, was not feasible at the time these experiments were performed. At any rate, one might at least speculate from these results, that iron shows a decrease in surface magnetization on hydrogen chemisorption, much as nickel does.

The observation of an effect by this experiment depends on the fact that an alternating field can penetrate a conducting sample only to a certain depth, known as the "skin depth." The experimental decrease in current strength with depth below the surface is given by the expression:

$$\frac{\text{Current at depth Z}}{\text{Surface Current}} = \frac{I_z}{I_s} = e^{-z/s} \tag{7}$$

where z is the depth below the surface and s is the skin depth. The power dissipated at depth z is proportional to the square of the current.

$$\text{Power at depth } z \propto \frac{I_z^{\,2}}{I_s^{\,2}} = e^{-2z/s} \tag{8}$$

The fraction of the total power dissipated in a depth z will then be

$$\frac{\int_0^z \left(\frac{I_z}{I_s}\right)^2}{\int_0^\infty \left(\frac{I_z}{I_s}\right)^2} = \frac{\int_0^z e^{-\frac{2z}{s}}}{\int_0^\infty e^{-\frac{2z}{s}}} = 1 - e^{-\frac{2z}{s}}$$

Apparently, about 90% of the power loss occurs in a skin depth, which for nickel is about 1000 Å at 10 KMc/sec., while about 35% is lost in the first 200 Å layer. From these figures, it does not appear unreasonable to expect to observe an effect of chemisorbed hydrogen on the surface, though the experiment is perhaps marginal.

Another consideration, however, may prevent any actual enhancement of sensitivity to hydrogen adsorption, through a skin depth decrease. The skin depth for a particular material is proportional to the square root of the ratio of the resistivity to the initial permeability of the material. If the adsorption of hydrogen involves the formation of a surface compound of low conductivity and low magnetic permeability, then the surface layers may not contribute a shielding effect for the microwave field at all and the effect of the chemisorption may be equivalent to merely removing a few layers of metal atoms from the crystal surface which of course should not effect the microwave losses. That both the conductivity and magnetic moment of the surface are reduced are shown by the results discussed in Chapter II. Thus, the lack of a large hydrogen effect on the

microwave losses in iron and nickel is consistent with the hypothesis that the formation of the metal hydrogen bond effectively removes the metal atom from involvement in the cooperative effects which are responsible for the large magnetic permeability and high conductivity of these metals.

IX. FERROMAGNETIC RESONANCE IN $Ni\text{-}SiO_2$ PREPARATIONS

A. EXPERIMENTAL

1. SAMPLE PREPARATION

The samples used in these experiments are the ones described previously on page (25). The reduction and pumping procedure was also the same as previously described. Samples of a few milligrams were used. The sample tube was a standard quartz EPR tube, fitted through a graded seal with a stopcock and a glass tapered joint, which allowed the sample to be removed from the vacuum line to the spectrometer. The tube could then be returned to the vacuum line for dosage with hydrogen or other treatment, as necessary.

2. SPECTROMETER

All spectra were obtained on a Varian V-4500 EPR spectrometer with 100 kc field modulation operating at a frequency of 9.5 KMc/sec. In order to reduce the time required to scan through the broad nickel resonance, the field scanning unit was modified by installing a 90 volt battery across the scanning helipot. This gave a maximum scan rate of 10^3 gauss minute. This sweep was found to be linear over a range from 50 gauss to 5000 gauss.

3. SIGNAL INTENSITY

The intensity of the ferromagnetic resonance signal was taken as proportional to the peak-to-peak height of the derivative curve of the absorption in all operations where the line width did not change. In other cases, the height times width squared was taken as proportional to the intensity on the assumption that the line shape did not change. Intensities were measured before and again after saturation of the sample with hydrogen for all samples described on page (25).

4. LINE WIDTHS

The line widths were measured peak-to-peak on the derivative of absorption curve. The field scanning rate was calibrated using the known hyperfine splitting of potassium peroxylamine disulphonate as a standard, or for very fast scanning rates, through the use of a rotating coil fluxmeter. The line width measurements are believed to be accurate within about $\pm$ 5%. Line widths were measured before and after hydrogen saturation for each sample.

5. SPECTROSCOPIC SPLITTING FACTOR

The spectroscopic splitting factor, or g-value, was measured before and after chemisorption of hydrogen for each sample. For some samples the absolute g-value was measured before and after chemisorption. As will be seen below the absolute determination of the

g-value requires the simultaneous measurement of the resonant frequency and the resonant field. Alternatively, the use of a standard sample of known g-value such as diphenyl picryl hydrazyl (DPPH) reduces the g-value determination to a field measurement only. Both methods were used in this study for the determination of absolute g-value. In the former case, the klystron frequency was measured by means of a cavity wavemeter, while the field was measured by a proton NMR fluxmeter. In the latter case DPPH was used as a standard and the field was again measured by the proton fluxmeter. In some, when it was only desired to determine whether or not the adsorption of hydrogen produced a g-value shift, the absolute g-value was not measured but the g-value difference between DPPH and the catalyst sample were measured before and again after chemisorption. For this purpose a small bit of solid DPPH was taped to the outside of the nickel sample tube so that the two signals could be recorded simultaneously.

B. RESULTS AND DISCUSSION

1. SIGNAL INTENSITY

The effects of various treatments on the intensity of the ferromagnetic resonance spectra of the Ni-SiO_2 samples described on page (25) were investigated. Such factors as heat treatment, length of time of reduction, method of sample preparation, and effect of

hydrogen, and oxygen were studied. The effect of hydrogen was of particular interest because of its relation to hydrogen embrittlement, corrosion, and the catalytic process. All of the samples previously described were studied and the experimental results for each of them will be summarized. A magnetic resonance spectrum consisting of a broad single line of g-value about 2.22 was found for each sample after reduction. That the resonance was due to nickel was confirmed by the similarity of the measured g-value to that found by other workers[26, 42] for nickel.

Sample I, the U.O.P. commercial preparation, gave a nickel resonance both before and after reduction. This sample is prepared for use in catalysis in such a way that the nickel particles are only superficially oxidized so the unoxidized nickel accounts for the pre-reduction resonance. Admission of hydrogen to a reduced and evacuated sample of this sample caused an approximately 6% decrease in resonance intensity. For this preparation it was found that the line also broadened considerably on admission of hydrogen. It was found that helium also caused a broadening of the resonance. If a few microns of helium were admitted, before saturation of the sample with hydrogen, the hydrogen caused no further broadening but only caused a decrease in intensity of 6%. This broadening effect is believed to be caused by cooling of the sample, which has been heated by the microwave power, by the admitted gas. Experiments to be described later show that increased temperature causes a narrowing of the resonance in

the U.O.P. sample. On admission of air the sample became quite hot and the resonance was no longer observed, due to oxidation of the nickel.

Sample II, the 9.8% Ni impregnation preparation gave a decrease in resonance intensity of 17 to 25%, averaging 18%. Admission of helium to this sample gave no effect. Figure 9 shows a typical spectrum obtained from this sample before and after saturation with hydrogen. Admission of air to this sample also caused the resonance to be lost. In order to place these results on a somewhat more quantitative basis and to determine whether the dependence of the signal intensity on the amount of hydrogen adsorbed was linear, as in the case of the static and low field measurements, and the radio-frequency loss measurements previously described, the fractional decrease in signal intensity was obtained as a function of the quantity of hydrogen adsorbed. The volumetric adsorption data could not be obtained directly due to the small size of sample required for the magnetic resonance analysis. However, a separate determination of the PV isotherm on a larger sample allows the volume adsorbed by the smaller sample to be determined from a measurement of the equilibrium pressure of hydrogen over the sample. Figure 10 shows a plot of signal intensity versus the volume of hydrogen adsorbed per gram of nickel. Unfortunately, only three points were available for this plot. However, the fact that the plot could be reproduced by taking care that the sample was treated in the same way for each

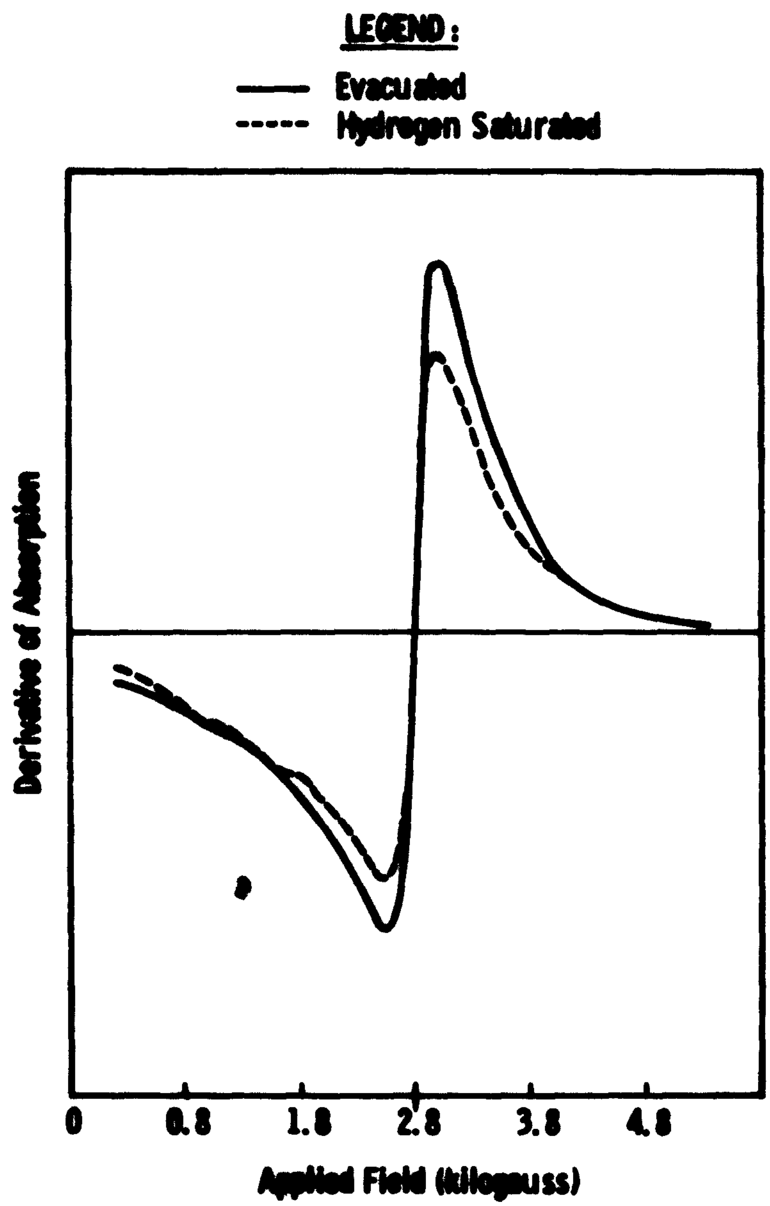


FIGURE 9
FMR SIGNAL FROM Ni - SiO_2 CATALYST (10% Ni)
REDUCED IN H_2 AT 350° C

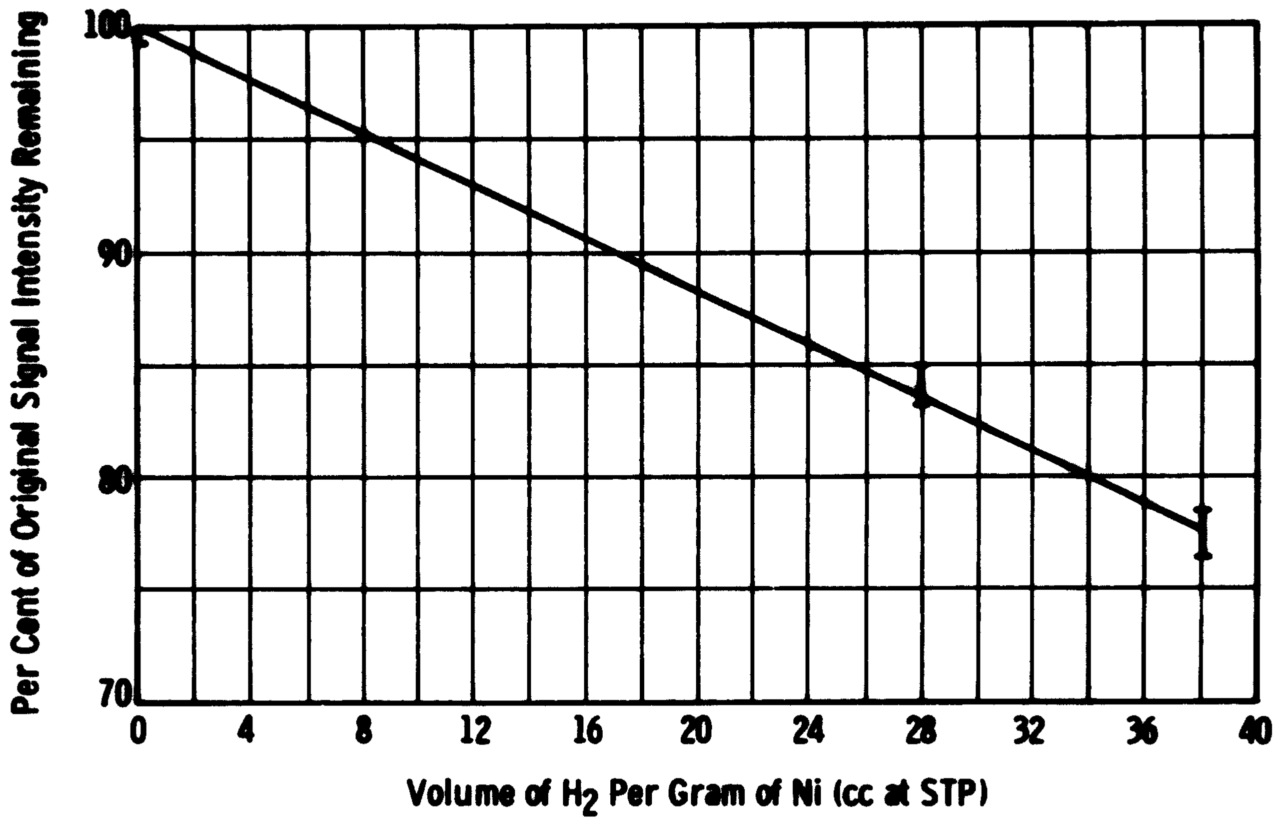


FIGURE 10
SIGNAL INTENSITY VS VOLUME OF HYDROGEN ADSORBED PER GRAM OF NICKEL

run, gives it some significance as an indication that the signal intensity does decrease linearly with the quantity of hydrogen adsorbed.

Samples I and II showed the decrease in signal intensity on adsorption of hydrogen after reduction periods of 12 to 17 hours at 350°C. In the case of Sample III, a 4.2% coprecipitated preparation, it was found that saturation with hydrogen produced a 23% decrease in signal intensity as shown in Figure 11, but only when the reduction was discontinued after two or three hours. When the sample was reduced overnight, as was the usual procedure, it was found that admission of hydrogen had no detectable effect. Furthermore, the admission of air had no effect and even heating at 300°C in a stream of oxygen gave no diminution of the signal intensity. The lack of effect by either hydrogen or oxygen seems to indicate that a long sojourn at high temperature in some way causes the nickel particles to become inaccessible. Other studies[4] have indicated that some of the nickel present in preparation such as these may be inaccessible to hydrogen, but no case of complete inaccessibility to hydrogen seems to have been reported. This effect will be discussed further below. The narrow signal, superimposed on the broad one, seen in Figure 11, is of uncertain origin. It occurs at a g-value of 2.00 and appears to be enhanced by heating of the sample under vacuum as well as under reducing conditions. A sample of pure silica prepared and treated in the same manner as the catalyst sample failed to develop a similar

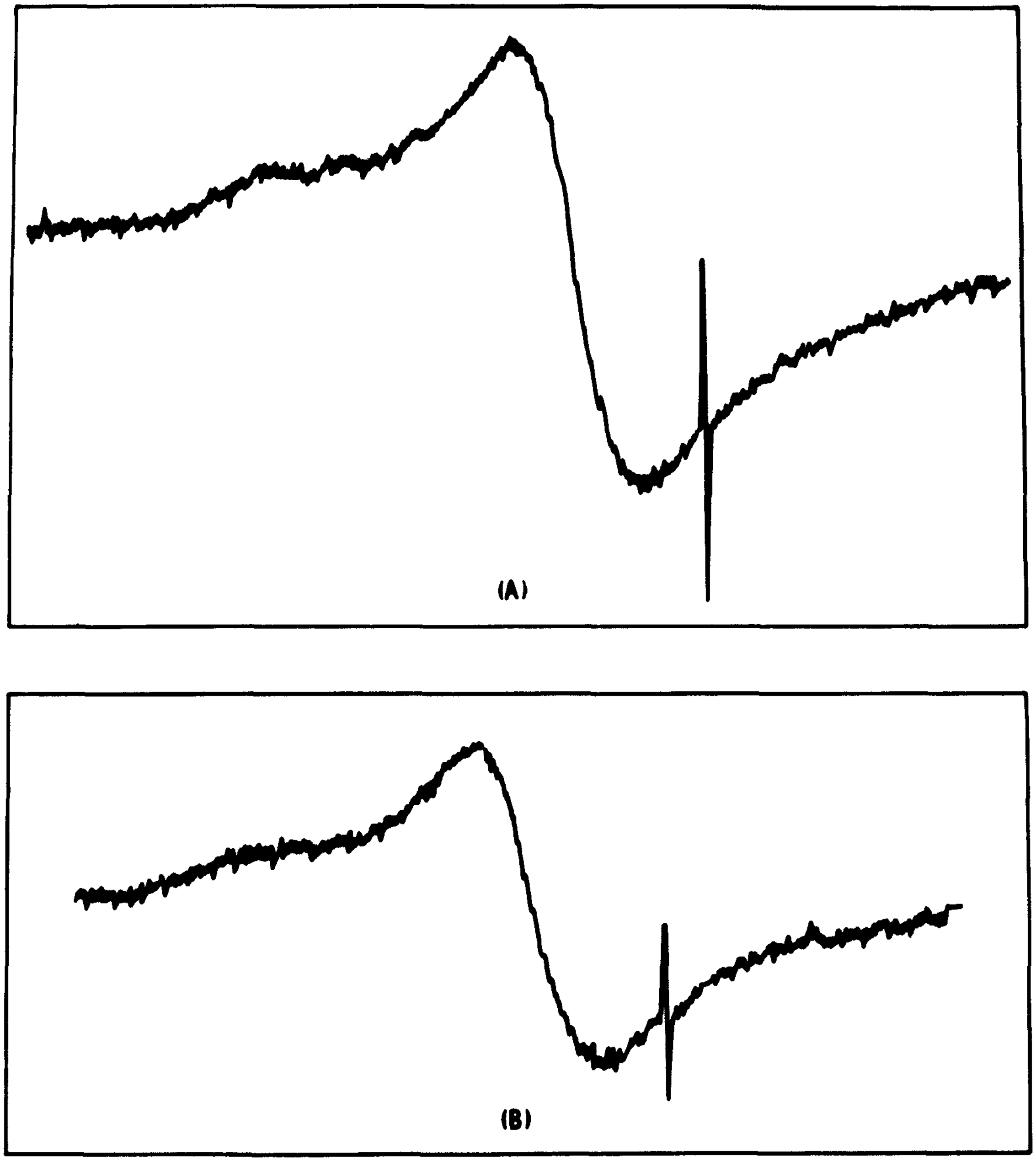


FIGURE 11
EFFECT OF HYDROGEN ON FMR SPECTRUM OF REDUCED $Ni-SiO_2$ CATALYST. "A" - EVACUATED, "B" - HYDROGEN ADMITTED (INSTRUMENT SETTING IDENTICAL FOR "A" AND "B")

signal, leading to the suspicion that the signal is somehow connected with the nickel. Figure 12 shows a more amplified view of the sharp signal before and after chemisorption of hydrogen. The width of the line has approximately doubled while the integrated intensity has remained constant to within the experimental error. A similar broadening of certain resonances found in finely divided carbon blacks by adsorbed oxygen or other paramagnetic gases suggested that the sharp signal was due to some organic impurity which was decomposed during the heat treatment of the catalyst, giving rise to a free radical. Since the hydrogen used here was purified of oxygen, however, it did not seem likely that a paramagnetic impurity was present. As a check, hydrogen from the storage bulb used in the nickel experiments was admitted to a carbon black sample known to be broadened by oxygen. No broadening was found to occur. The explanation of this effect is not known.

Samples IV and V were low nickel samples ($\sim$ 1%) prepared by impregnation and coprecipitation, respectively. These samples were prepared in an effort to produce very small particles of nickel which might lose all of their magnetization when saturated with hydrogen. Sample IV, the impregnation catalyst showed an approximately 10% decrease in signal intensity on hydrogen saturation if it was reduced for twelve hours, when reduction was stopped after only two hours, a 20% decrease was observed. In the case, of sample V, the coprecipitated preparation, no effect was observed on admission of

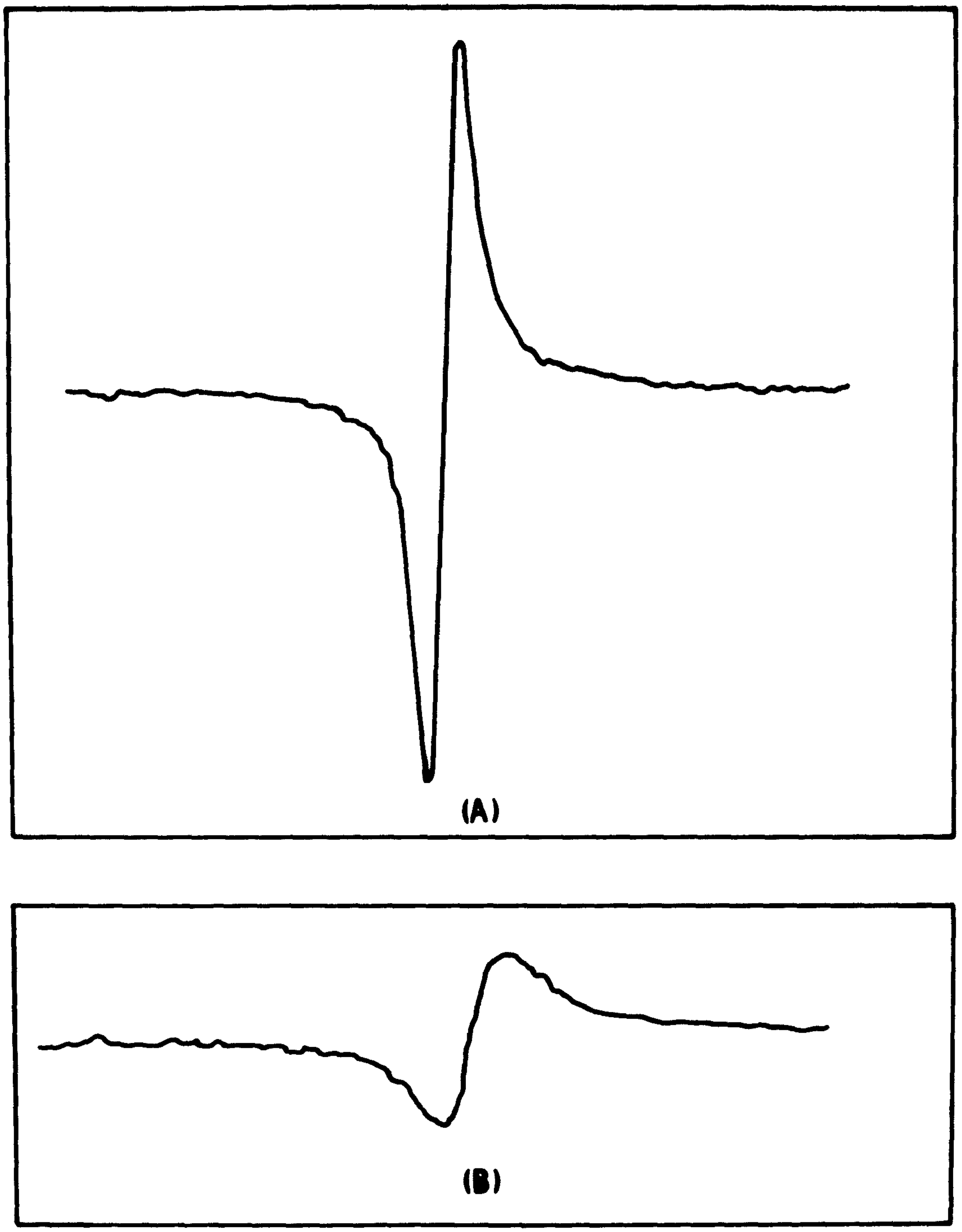


FIGURE 12
EFFECT OF HYDROGEN ON SHARP RESONANCE IN Ni-SiO_2 CATALYST
(INTEGRATED INTENSITIES OF "A" AND "B" ARE NEARLY EQUAL,
BUT THE LINE WIDTH OF "B" IS APPROXIMATELY DOUBLED BY THE
ADMISSION OF HYDROGEN)

hydrogen regardless of the time allowed for reduction.

The decrease in signal intensity is thought to be a direct result of the change in magnetization of the sample. The signal intensity is, of course, proportional to the net magnetization of the sample. As a method for measuring the effect of adsorbed hydrogen on nickel particles, the resonance method is equivalent to the static field method, but it measures the magnetization much more sensitively. Thus, no increase in sensitivity in terms of the fractional loss of magnetization is gained, as is the case in the radio-frequency loss measurements described earlier, but only an increase in the sensitivity to the amount of nickel present. Thus, the resonance method has advantages where it is desired to study preparations containing small quantities of nickel, or for measurements at high temperatures where very small particles have lost nearly all of their magnetization. For example, the greater sensitivity should make possible the simultaneous measurements of magnetic changes in the adsorbent and infrared absorption spectra of the adsorbate.

The lack of any effect of either hydrogen or oxygen on the resonance of Samples III and V suggests that the nickel particles in these samples are situated in such a way that they are inaccessible to these gases. The only exception to this was that Sample III showed an effect when reduced for only two hours. This result and the fact that the 1% impregnation catalyst, Sample IV, showed a diminishing hydrogen effect on longer reduction suggests that the

reduction process leads to less accessibility of the nickel particles. Similar indications of inaccessible nickel have been obtained on preparations similar to these by Schuit and van Reijen[5] who compared the experimental amounts of hydrogen adsorbed with that predicted on the basis of the magnetically determined particle size distribution of the sample. In every case, the experimental value was lower than expected. Results by Sabatka and Selwood,[38] in which U.O.P. catalyst was treated with CO to remove the larger particles, also gave a low hydrogen adsorption, which could be interpreted in terms of inaccessibility of the smaller nickel particles to hydrogen.

Schuit and van Reijen[5] have suggested a mechanism for the formation of a protective silica "skin" over the nickel particles during reduction, which is based on the assumption that the coprecipitate consists of nickel silicate, $Ni-O-Si(OH)_3$, so that even prior to reduction there is a high concentration of silica on the nickel oxide surface. According to this interpretation the protective effect is closely connected with the coprecipitation method of preparation.

This interpretation is consistent with the results of the present work, in that the coprecipitate samples containing large amounts of silica showed complete inaccessibility. However, even the impregnation catalyst containing 1% nickel showed inaccessible nickel when reduced for several hours even at the relatively low temperature of 350°C. Apparently it is possible for the silica to

sinter around the nickel particles even in the case of impregnation catalysts. It should be mentioned that Samples III and V, when reduced for about 17 hours do not show catalytic activity for the hydrogenation of benzene to cyclohexane. This result is based on a single experiment in which benzene saturated hydrogen was passed slowly over the previously reduced catalyst at 125°C and the resulting gases were condensed for analysis by NMR. Such a result is not surprising as it merely confirms the idea that hydrogen adsorption is a necessary step in the catalytic process.

2. G-VALUE

Most investigations in the field of ferromagnetic resonance have employed plane samples and measured the microwave absorption with the static and microwave fields mutually perpendicular and tangential to the plane of the sample.[42, 43, 44] The use of plane samples has considerable disadvantage since, according to equation (2), it is necessary to know the saturation magnetization and the appropriate demagnetizing factors under the actual conditions of the experiment in order to determine the g-value. In addition, it is difficult to take into account effects arising from magnetic anisotropy for a polycrystalline sample in which the individual crystallites are interacting strongly. The g-values and line widths derived from experiments on plane samples are therefore subject to some uncertainty.

In order to overcome the difficulties involved in the use of plane samples, Bagguley has used an alternative method in which the sample is a dilute suspension of spherical particles having dimensions small compared with the skin depth at microwave frequencies. For particles of this type, the theory of ferromagnetic resonance developed by Kittel,[27] Polder,[28] and Van Vleck[29] applies rigorously, and the ferromagnetic resonance equation giving the resonant frequency, ν, in terms of the applied external field, H_z, becomes,

$$h\nu = g\beta H_z,$$

if anisotropy terms are neglected. The g-value and the line width can now be obtained without assumptions regarding the saturation magnetization and the demagnetizing factors.

Bagguley has studied samples of small nickel particles (also iron, cobalt, and various alloys), prepared by centrifuging suspensions of the finely divided metal in paraffin. The particles were obtained from reduction of nickel carbonyl and formate or by an arc discharge between nickel electrodes, and were believed to have diameters in the range from 50 to 100 Å, although no direct evidence for particle sizes was obtained. Since the skin depth for nickel is about 10^{-5} cm at microwave frequencies, particles of 50 to 100 Å diameter should be sufficiently small to allow equation (1) to be applied. Bagguley's samples finally contained of the order of one microgram of nickel, leading to problems of sensitivity.

In the present work, the g-values and line widths of the nickel ferromagnetic resonance have been determined for nickel-silica preparations containing varying proportions of nickel. These samples are believed to have the following advantages over those used by Bagguley:

(1) The average particle size for two of these samples is known from magnetic measurements[30,45] and for other samples similarly prepared have been determined directly by electron microscopy and by a magnetic method.[4] The results indicate that the particle sizes range from radii of about 10 to 80 Å with the majority of the nickel mass present as particles of 10 to 30 Å radii.

(2) These preparations are quite stable with respect to agglomeration of the particles, temperatures of about 450° or more for several hours being required to cause sintering to occur. The samples can therefore be cleaned by a process of heating and pumping after reduction, thus reducing the possibility of surface impurities affecting the g-values or line widths. Also, the stability of the sample

allows a higher concentration of nickel to be used, giving a resonance signal sufficiently strong to allow accurate g-values and line widths to be determined.

(3) The slow reduction procedure at 350°C might be expected to lead to a minimum of strain in the crystal structure of the nickel, thus reducing any effects of strain on the line width.

The results of this study then will provide a check on the results of Bagguley and other workers.

In addition, the measurement of the g-value before and after chemisorption can shed some additional light on the nature of the nickel-hydrogen bond. In order to indicate how this might be so, it seems desirable at this point to discuss briefly the significance of the g-value.

The spectroscopic splitting factor, g, is an important quantity because it provides a measure of the relative contributions of the spin and orbital angular moments to the magnetic moment; therefore, the g-value gives an indication of the electronic state of the magnetic carriers. If the magnetic moment of an atom is

$$\mu = (L + 2S)\beta$$

where L and S are the orbital and spin angular momentum operators, respectively, and β is the Bohr magneton, "g" is then defined by treating the magnetic moment as though it arose from spin only, i. e.

$$\mu = (L + 2S)\beta = g(S)\beta \, .$$

Thus, for a "free" electron spin, g = 2.0, and any deviation from this value indicates the magnitude of the contribution of the orbital angular momentum to the magnetic moment.

In the case of the nickel-hydrogen system, the effect of chemisorption of hydrogen on the g-value might indicate whether or not the nickel-hydrogen bond is localized. If the chemisorption bond between the hydrogen and the surface nickel atoms is localized, it would be expected that the nickel atoms involved would no longer participate in the metallic system and the effect on the magnetic properties of the particle might be approximately as though a part of the metal had been removed. The observed g-value would not be expected to change in this case but would still be that of metallic nickel.

If, on the other hand, the nickel-hydrogen bond is not localized, then the perturbation of the hydrogen on the nickel atom may be transmitted throughout the metallic system, altering the energy levels of the system and producing a g-value shift. (See also Dietz, Reference 30.)

The g-value determinations on the five nickel silica preparations studied, were found to be 2.22 $\pm$ .02 which agrees very well with the values obtained by Bagguley[26] and other workers.[42] Hydrogen chemisorption had no observable effect on the g-value. This observation is consistent with the formation of a localized nickel-hydrogen bond as discussed above. Theoretical work by Grimley[46] and Koutecky[47] based on a molecular orbital calculation for the chemisorption bond, support the hypothesis that the nickel-hydrogen bond is localized, and that the nickel atom involved in the bond as well as some of its neighbors are removed from the cooperative structure of the metal. Such a picture, then, is consistent both with the lowering of the magnetization and the lack of g-value shift on chemisorption.

3. LINE WIDTHS

Measurements of line widths for the nickel-silica preparation described here give the values shown in Table III at room temperature. The table also includes the results obtained by Bagguley and Harrick,[48] on what they believe to be colloidal nickel particles suspended in paraffin. The line widths given here are the measured separation in magnetic field between the points of maximum slope on the absorption curve. Note that the values obtained here are only about half those obtained by Bagguley and Harrick.

TABLE III

LINE WIDTHS FOR SILICA SUPPORTED NICKEL

Sample	Line Width (Gauss)	Particle Radius (Average)
I (U.O.P.)	580	65 Å
II (10% Impreg.)	520	15 Å
III (4.2% Coppt.)	350	Unknown
IV (1% Impreg.)	310	Unknown
Ni in Paraffin	1000	25 Å
(Bagguley & Harrick)		

The reason for the variation in line width from one sample to another is not known, but it may be related to the particle size distribution. Were this true, it would indicate that the particles obtained by Bagguley were considerably larger than expected. Another indication that Bagguley's particles were much larger than expected is that he made no mention in his papers on this subject of observing superparamagnetic behavior of the particles on raising the temperature. Particles of 25 Å radius are well within the superparamagnetic size range for nickel. An assemblage of such particles would lose a considerable fraction of their saturation magnetization even at room temperature, while at 5-600°K as the Curie temperature is approached less than 10% of the saturation magnetization might remain. Bagguley's samples were estimated to contain only about a μ gm of nickel, so that there was some difficulty with sensitivity problems, making it necessary even to purge the

atmospheric oxygen from the cavity to avoid its interference. The magnetic resonance signal from such a small quantity of nickel would almost certainly not have been detectable at temperatures around $600^{\circ}K$, as found by Bagguley and Harrick.

The lack of agreement between the line widths obtained in this work and those obtained by Bagguley and Harrick might also be accounted for in terms of a difference in magnetic anisotropy or surface contamination between their samples and the ones used here.

Van Vleck[49] has shown that for an assembly of randomly oriented, non-interacting spherical crystallites, the effect of magnetic anisotropy is to broaden the resonance line and to shift the resonance peak. The order of magnitude of each effect is $K_1/2M_s$, where K_1 is the first order anisotropy constant and M_s is the saturation magnetization. Though K_1 describes the magneto-crystalline isotropy only, magnetic anisotropy from any source can be expected to effect the line width. If the particle is formed under conditions which produce strains in the crystal structure, then a higher anisotropy and hence a greater line width can be expected. If the particles are not spherical, shape anisotropy can also contribute to the line width. Impurities present in the particle will also contribute to the line width.

Since the catalyst samples used here are known to consist of particles of dimensions much less than the microwave skin depth,

since similar samples have been shown to contain nearly spherical particles and since the method of preparation would be expected to lead to a clean, unstrained particle, the line widths reported here are probably more meaningful than the ones reported by Bagguley and Harrick. It is interesting to note that the line widths found here for the dilute nickel samples, III and IV, are only about half of the single crystal value of 350 gauss half width which Bagguley and Harrick[48] deduce from the approach of the line width to this value at high temperatures where the anisotropy effects are smaller. They may indicate that the particles present in the nickel-silica preparations are highly isotropic so that virtually no broadening from this source arises and that also particles of this small size no longer behave as ordinary crystals and thus give a line width smaller than a somewhat larger single crystal might. The larger line widths for the more concentrated Samples I and II may arise from increased particle size or from an interparticle interaction of some kind owing to the greater concentration of particles.

X. SUMMARY

The effect of chemisorbed hydrogen on the magnetic losses of a typical nickel-silica preparation has been investigated at frequencies of 3.7 and 13 Mc/sec. An increased sensitivity to the effect of hydrogen over the effects observed at static and low frequency fields has been obtained. This increase in sensitivity has been interpreted as due to a variation in relaxation times for ferromagnetic particles as described by the equation of Neel for the relaxation time. This phase of the work apparently has opened a new method for studying the so-called "activated" adsorption of hydrogen.

Experiments designed to detect the effect of adsorbed hydrogen on bulk nickel and iron samples by taking advantage of the small skin depths at microwave frequencies have been described. A discussion of the possible reasons for the lack of a clear-cut effect is given.

A study of the ferromagnetic resonance spectra of several nickel-silica preparations has been made. Measurements of the nickel g-value and line width have been made and compared to the results of other workers. The g-value of $2.22 \pm .02$ obtained here agrees well with that obtained by other workers for nickel. The line widths obtained, however, are smaller by a factor of about two than

those obtained by other workers. Possible reasons for this discrepancy have been discussed. The effect of chemisorbed hydrogen on the g-value, line width and intensity of the nickel ferromagnetic resonance is determined, and the results are discussed in terms of such factors as particle size, accessibility of the particles to hydrogen, and the degree of localization of the chemisorption bond. It has been demonstrated that substantially the same effects observed in static and low frequency studies of the magnetic changes occurring on chemisorption can be observed by the magnetic resonance technique and with much greater sensitivity in terms of the amount of nickel required.

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